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CONSULTING ANALYTICAL SERVICES INTERNATIONAL

2804 EAST BATTLEFIELD, SPRINGFIELD, MISSOURI 65804, 417-882-1017, 1018

Report On

PRETREATMENT PROCESS
CONSIDERATIONS

for

DUGAN and HELTERBRAND COMPANY, INC.

Marshfield, Missouri



S00048597
SUPERFUND RECORDS

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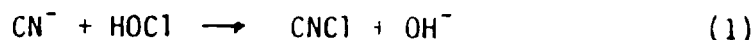
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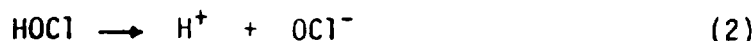
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The reduction or elimination of cyanide in a wastewater is most often accomplished by the method of alkaline chlorination. Most references which relate any information in regard to this method, have very similar wording which may be summarized as follows:

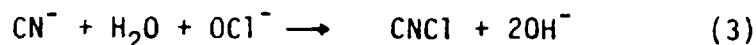
In the alkaline chlorination of cyanide, the first reaction product is cyanogen chloride according to the reaction:



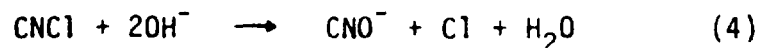
(Note: above pH 9 to 9.5, hypochlorous acid, HOCl, is almost completely dissociated in water to hypochlorite ion,



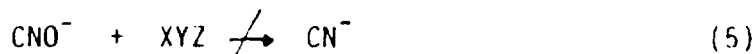
so that equation (1) above is more properly written:



The first reaction is fast, and the cyanogen chloride, CNCI, produced may exceed the toxicity of an equal concentration of cyanide. At alkaline pH, cyanogen chloride hydrolyzes to cyanate ion



but the reaction is relatively slow, being pH and time dependent. At a pH of 9, with no excess of chlorine present, cyanogen chloride may persist for 24 hours. Once the hydrolysis in equation 4 has taken place, however, there is no known natural reduction reaction which may convert the cyanate back to cyanide, i.e.:



Equation 5 is not known to exist.

In applying the above equations for the destruction of free cyanide, to the problem of complex cyanides, some additional considerations are necessary. While equation number 3 is again a relatively fast reaction, it is dependent upon the dissociation constant of the cyanide complex, which also plays a role in its toxicity. Two other literature citations summarize the information obtained to date:

"Metal cyanide complexes such as nickel, cobalt, silver and gold do not dissociate readily. The chlorination reaction therefore requires more time and a significant chlorine excess. Iron cyanides are not oxidized by chlorination."⁽¹⁾

"...some of the metal cyanide complexes cannot be treated rapidly with the usual chlorination. Nickel and silver cyanides for example, require a long time for treatment and as the soluble free cyanide is destroyed in the chlorination, there is danger that the metal cyanides will precipitate as the insoluble salts and become available for further chemical destruction. Sludges containing slowly soluble metal cyanides would then result, making solid waste discharged by the plant unsuitable for land disposal."⁽²⁾

In the same reference as immediately above, a typical batch treatment is shown and described which calls for a 45 minute circulation time after the addition of the hypochlorite. This time is apparently sufficient in the straight forward chlorination of free cyanide, and represents the "slow" reaction time. It is apparently not a measure of the time realistically required for treatment of a metal complex cyanide, and especially for one of the specific metal complexes designated as being more of a problem, e.g., silver. The outline on the next page gives a tentative

- (1) Standard Methods for the Examination of Water and Wastewater, 15th Ed., Published jointly by A.P.H.A., A.W.W.A., W.P.C.F., Washington, D.C. (1981).
- (2) Waste Treatment-Upgrading Metal-Finishing Facilities to Reduce Pollution, U.S. Environmental Protection Agency, Technology Transfer Series, Publ. No. EPA 625/3-73-002, Washington, D.C. (1974).

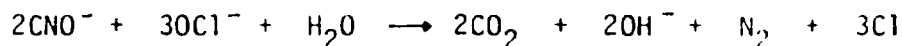
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TENTATIVE PROCESS OUTLINE

After removing concentrated silver cyanide complex for plating:

1. Add water rinse to tank. Volume should be about 2000 to 2200 gallons.
2. Adjust pH to about (optimum pH not established yet)
3. Allow to stand about (time required not determined)
4. Draw water off for either use in another tank, or for plating as appropriate. Rinse water should be reusable to some extent. In one test, the rinse picked up 4400 ppm cyanide and about 26 ppm silver. The pH was 10.96. Extensive reuse would undoubtedly reach a point of diminishing return. Testing may indicate the optimum number of tanks that the rinse could be used in before it is subjected to plating. After plating, use it as make-up water for the sodium cyanide, or use it again in the rinse process.
5. Add an additional $2000 \pm$ gallons of water to tank.
6. Add approximately 6 to 7 gallons (current estimate) sodium hypochlorite solution, NaOCl, at a strength of about 10% available chlorine to the tank. (Nominal 10% is as purchased).
7. Adjust the pH to 11.5 if it is lower than that.
8. Circulate or mix tank for about 24 hours. The contents of the tank at this point should be reusable at step five in another tank. Again, as in the rinse water, there may be a limit to the number of uses, due to the increasing concentration of cyanate, but the reaction:



may occur to some extent even at elevated pH, thus removing some excess cyanate from the solution. When the solution's use is exhausted, it may be discharged into the municipal sanitary sewer system. (Some initial testing should be done to confirm levels of contaminants, reuse ability, and suitability for discharge).

9. When the liquid contents of the tank are removed, the tank should be opened for the first time since charging it with film, and the residue of chips should be suitable for land disposal.

procedure. I would label it as tentative in that only a limited number of analyses have been performed to characterize the levels of cyanide, and a standard procedure should be based on the full anticipated range of values. But once established, an adequate feed-rate for chemical addition can be set up which should ideally only require a small number of process control samples in the future. You may find that periodic sampling to document the destruction of cyanide is both necessary and desirable. In fact, the municipal sewer authority may require at some time that you do. A reasonable suggestion would be that you might sample once each 2 weeks, simply as a control measure to maintain adequacy of the process and of your documentation. It's a good guess that some regulatory agency, sometime, will want to review the control data you generate, and it would be best to already have it instead of being surprised. Estimated cost for one analysis every other week would be less than \$450.00 annually.

Estimated chemical usage was done using both sodium hypochlorite, NaOCl , and calcium hypochlorite, $\text{Ca}(\text{OCl})_2$. It would appear that it is far more economical to use the sodium than the calcium, even though the nominal percentage of available chlorine is 65 to 70% with the calcium hypochlorite, and only about 10% with the sodium. Estimates are based on the cost figures and calculations on the next two pages.

Following the Tentative Process Outline should accomplish several things. First, the additional rinse may pull out as much as another one-half to one pound of silver from each tank. Second, the additional rinse could provide some savings in the amount of sodium cyanide required, as the rinse is nearly $\frac{1}{2}\%$ cyanide and could be used as make-up water for the cyanide solution immediately after the rinsing operation, or after several rinsing operations and subsequent plating of the accumulated silver. Third, the utilization of the rinsing operation wash changes the definition of when the film chips become a waste. As long as there is recoverable and reusable cyanide and silver in the chips, and an attempt to extract these materials for legitimate use is made, then the chips are clearly defined as a process intermediate. Fourth, the process of silver

CALCULATIONS

1. Without Water Rinse

Cyanide Concentration = ± 5600 ppm = ± 22.4 lb per 4000 lb charge

Allowing 10% Contingency \pm = 25 lb cyanide per tank

At nominal dosage of 1.45:1 available chlorine: cyanide,

requirement of 36.25 lb available Cl to destroy 25 lb CN

Allowing about 10% contingency for excess, requirement is ± 40 lb./tank

2. With Water Rinse

Cyanide Concentration = ± 800 ppm = ± 3.2 lb per 4000 lb charge

Allowing 20% Contingency \pm = 4.0 lb cyanide per tank

At nominal dosage of 1.45:1 Available chlorine: cyanide,

requirement of 5.8 lb available Cl to destroy 4 lb CN

Allowing about 10% contingency for excess, requirement is ± 6.5 lb./tank

COST

Chemical Form		ChemTech	McKesson
Size		Tom Richardson	Bud Norton
Calcium hypochlorite	$\text{Ca}(\text{OCl})_2$	Available Chlorine - 65% \pm	
100 lb drums - 3 - 4 drums	-		\$145.65/drum
5 - 19 drums	-		142.75/drum
20 - > drums	-		137.75/drum
truckload (> 25,000 lbs)	\$125.00/drum		118.40/drum
truckload (> 38,000 lbs)			116.61/drum
Sodium hypochlorite	NaOCl	Available Chlorine - 10% \pm	
55 gallon drums 2 - 3 drums	-		1.035/gallon
4 - 9 drums	-		.885/gallon
10 - > drums	± 1.00 /gallon		.835/gallon

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COST, Continued

Cost per available pound of chlorine:

Calcium hypochlorite (65% available)
nominal cost @ \$120.00/100 lbs. ... \$ 1.85/lb

Sodium hypochlorite (10% available, 10.636 lb/gal)
nominal cost @ \$1.00/gallon ... 0.94/lb

At a requirement of 6.5 lb chlorine per tank:

Sodium hypochlorite @ 10% available chlorine
Total use 65 lb/tank as NaOCl Solution = $\pm 6 - 6.5$ gallons/tank
@ 1.00/gallon = $\pm \$6.00 - 6.50$ /tank

Calcium hypochlorite @ 65% available chlorine
Total use 10 lb/tank as $\text{Ca}(\text{OCl})_2$ ± 10 lb/tank
@ 120.00/Cwt = $\pm \$12.00$ /tank

Advantages

Disadvantages

NaOCl

About $\frac{1}{2}$ cost wt/wt
Liquid - easy to feed

Loses strength on standing
More Volume Require, Storage
Less Available Chlorine

$\text{Ca}(\text{OCl})_2$

Solid, Takes Less Volume
More available chlorine

Does not lose strength

About 2X Cost wt/wt
More difficult to feed in
closed system
Susceptible to spontaneous
heating, fire and
explosion if contam-
inated by organics
More Difficult to Handle

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and cyanide recovery, followed by alkaline chlorination, all carried out within a closed process tank, should qualify as one of the specific exclusions allowed within the regulatory framework promulgated from the Resource Conservation and Recovery Act, and its Hazardous Waste Management provisions. "A hazardous waste which is generated in a...manufacturing process unit...is not subject to regulation under Parts 262 through 265 and Parts 122 through 124 of this chapter or to the notification requirements of Section 3010 of RCRA until it exits the unit in which it was generated..." (40CFR Part 261, § 261.4(c)). Similarly, the described process arrangement of treatment totally within the confines of the closed manufacturing process unit should also qualify as a specific exemption from the regulations of the Missouri Hazardous Waste Management Law, i.e., the process meets the definition of a totally enclosed treatment facility. (10CSR 25-7.011(1)(C) and 10 CSR 25-3.010(1)(T)3). After all process operations are complete, the first time that the tank is opened is coincidental with the first time that the film residue is defined as waste, and while it is a solid waste, it should not meet the criteria in the regulations to define it as hazardous. And finally, the process operation of mixing of the tank contents with alkaline hypochlorite, followed by separation of the liquid and solid phases and subsequent discharge of the liquid phase to the sanitary sewer system, is clearly defined as a Pretreatment operation. Discharges to a municipal sanitary sewer, from which the ultimate discharge is controlled by a permit issued pursuant to the N.P.D.E.S. authority, which is in compliance with applicable pretreatment standards, is specifically excluded from regulation under the Hazardous Waste Management Programs. The residues (sludges, etc.) created by pretreatment processes may be subject to Hazardous Waste rules, but as mentioned previously, the residue of film chips remaining after separation of the liquid and solid phases, fails to meet the criteria in the regulations which would define it as hazardous. A process which is clearly subject to Pretreatment regulations, as defined under Title III of the Federal Water Pollution Control Act as Amended by the Clean Water Act,

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and not subject to the Subtitle C (Hazardous Waste Management) Regulations of the Resource Conservation and Recovery Act should save the company substantially in both time and expense. The process should not cause the company to qualify as a Hazardous Waste Generator, subject to the provisions of 40CFR Part 262, and most importantly, would not subject the company to the Facility Regulations in 40 CFR Part 264, with the full measure of the financial responsibility requirements including liability insurance bond, facility closure requirements, and post-closure trust fund.

